

# REPORT DOCUMENTATION PAGE AFRL-SR-BL-TR-99-

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1. REPORT DATE (DD-MM-YYYY) 17-05-1999		2. REPORT DATE May 17, 1999		3. DATES COVERED (From - To) 3/1/96 - 2/28/99	
4. TITLE AND SUBTITLE Development of Some Promising Approaches for the Toughening of High-Temperature Polymers				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-96-10052	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) C. Kumudinie, J. K. Premachandra, J.E. Mark, M.R. Unroe, and F.E. Arnold				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Cincinnati Cincinnati, OH 45221-0172				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Directorate of Chemistry and Life Sciences AFOSR/NL, Room 732 801 North Randolph Street Arlington, VA 22203-1977				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT Unlimited					
13. SUPPLEMENTARY NOTES None					
14. ABSTRACT A number of polymers of interest and importance to the U. S. Air Force have a degree of brittleness that limits their utilization. This brittleness was reduced, and a number of othe physical properties improved, by the in-situ introduction of dispersed elastomeric phases. The approach was a modification of the sol-gel technique previously used to introduce much harder ceramic-like phases into similar polymers. Specifically, precursor molecules were chosen so that their hydrolyses did not produce a ceramic such as silica, but one in which organic groups flexibilize the phases. This increases extensibility and thereby toughness, and has some additional benefits such as decrease of water absorption.					
15. SUBJECT TERMS High-temperature polymers, toughening, silica, composites, elastomeric phases, fracture, mechanical properties, water absorption, transparency					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT None	18. NUMBER OF PAGES This form plus 5	19a. NAME OF RESPONSIBLE PERSON J.E. Mark
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (513) 556-9292

PI: Mark, James E.

Institution: University of Cincinnati

Grant: F49620-96-10052, "Development of Some Promising Approaches for the Toughening of High-Temperature Polymers".

## 1. SUMMARY OF RESEARCH

Some high-temperature polymers, specifically two poly(arylene ether)s (6F-ETPP-E and FEK-E) and a hydroxy-functionalized polybenzoxazole (HPBO) copolymer, were toughened using dispersed rubbery phases within the polymer matrix. These rubbery phases were generated in-situ via the sol-gel process. In the case of HPBO, strong bonding between the organic and inorganic phases was achieved using the bonding agent isocyanatopropyltriethoxy silane. A series of samples were prepared with a fixed amount of the dispersed phase generated using different combinations of sol-gel precursors, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS) and dimethyldimethoxysilane (DMDMOS). Hydrolyses of these two precursors gives silica-siloxane phases with hardnesses intermediate to the very hard silica and the much softer polysiloxane. The optimal molar ratio of the sol-gel precursors which gave the desired properties was used to prepare samples with varying amounts of the dispersed phase. The resulting samples were characterized with regard to their transparency, morphology, mechanical and thermal properties, and the extent of water absorption. The clarity observed for the samples indicated good dispersions of the rubbery second phase and the scanning electron micrographs showed uniformly dispersed particles. For the poly(arylene ether)s, a significant increase in toughness and ultimate elongation were achieved for samples prepared from relatively large amounts of sol-gel precursor containing the larger number of alkyl groups. In HPBO samples having low levels of the rubbery phase, both toughness and ultimate elongation were increased without causing any significant change in the modulus with increase in the amount of rubbery phase. Improvements in these properties of the HPBO polymer are rather large compared to those for the poly(arylene ether) polymers. The results also demonstrated improved thermal properties and decreased water absorption of the composites.

The above technique was also applied to successfully toughen another polymer in the poly(arylene ether) family, poly(biphenyl ether triphenyl phosphate) (PBETPP). The solubilities of PBETPP were found to have been greatly improved by sulfonation. In order to prevent macro-phase separation, strong interactions between the organic and inorganic phases in the PBETPP/silica-siloxane composites was introduced by addition of N,N-diethylaminopropyl-trimethoxysilane (DEAPTMOS). The extensibility of the toughened PBETPP was found to increase significantly with increase in the amount of silica introduced. For example, the composites had a 20 % extensibility when the content of silica was 8 %. Also of importance, the glass transition temperature decreased only slightly.

In a related study, aerogels were prepared so as to have a hybrid structure, by carrying out the supercritical drying process on composites consisting of an in-situ generated silica network as the inorganic phase and a high-temperature polymer as the organic phase. The goal was to maintain the best properties of

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both components, for example, decreasing the brittleness of the ceramic phase with the polymeric phase. A poly(benzobisthiazole) of very high thermal stability, with sulfonation to increase its reactivity, was chosen for the organic phase, and it was bonded to the silica phase by the silane coupling agent N,N-diethylaminopropyl trimethoxysilane. A range of polymer/silica compositions was investigated, and the resulting materials were characterized using small angle x-ray scattering, N<sub>2</sub>-absorption measurements and transmission electron microscopy. The values of Young's moduli obtained from the initial slopes of the compressional stress-strain curves decreased with increase in the amount of polymer present in the aerogels. According to the compressional stress-strain results, the deformability of silica aerogel is significantly increased by the incorporation of organic polymer into the inorganic silica network structure. Values of Poisson's ratio were also determined and used to estimate longitudinal sound velocities, which can be important in some applications of aerogel materials in general.

A polyamide or "Nylon" having a silane coupling agent as the side chain was synthesized by reacting a commercial Trogamid sample and an epoxysilyl compound, using triethylenediamine as catalyst at 50-60 °C for 3 days. The dried films exhibited some improved ultimate properties, including toughness, at lower epoxysilane contents. In particular, the tensile strengths of the samples that were annealed at 120 °C were greatly improved. For the polyamide-epoxy composites with a difunctional silane, the maximum extensibility was increased by increasing the silane content, but at the cost of decreasing tensile strengths. For the sample with 20 % difunctional silane (relative to the amount of silica), the tensile strength was still high and the toughness was greatly improved. For the 20 and 40 mole % polyamide-epoxysilane composites with 20 % difunctional silane (again relative to the amount of silica), the 40 mole % sample had higher tensile strength but less toughness than the 20 mole % sample. The Trogamid and an isocyanatosilyl compound were also reacted under the same conditions but only the isocyanate groups reacted with the polyamide end groups (carboxylic acids and amines). The dried films showed properties similar to those of the polyamide-silica hybrid materials with tetraethoxysilane. The tensile strengths of the polyamide-isocyanatosilane composite with trifunctional silane increased somewhat, but at the cost of decreased toughness. Overall, the results provided guidance on how to optimize the properties of an important polyamide for a given specification of applications.

For purposes of comparison, some composites were also prepared by blending fumed silica into the polyamide, both with and without a coupling agent. These more common-place materials were similar to the polyamide-silica composites reinforced by in-situ produced phases. Those without a coupling agent, however, had lower increases in tensile strength (typically around 10 % compared to 25 %). Scanning electron micrographs of these composites showed non-adhering silica particles in relatively large agglomerates. Including a bonding agent increased tensile strengths and produced evidence for better adhesion between the organic and inorganic phases.

The most significant accomplishments were successfully improving some of the mechanical properties of high-temperature polymers of interest to the US Air Force.

## 2. PROGRAM STATISTICS

(1) Number of PI's and Co-PI's:

One: J. E. Mark

(2) Number of Postdoctoral Students Supported in the last 36 months under AFOSR:

One: Y. W. Park

(3) Number of graduate students supported in the last 36 months by AFOSR: Ten:

J. Braun

C. Kumudinie

R. Patil

J. Premachandra

G. Rajan

M. Sinha

H. Sun

B. Viers

R. Zhang

W. Zhou

(4) Other researchers supported in the last 36 months by AFOSR:

One Visiting Scientist: B. Erman

(5) Number of publications in refereed journals in the last 36 months: 75

(6) Number of publications in refereed journals in the last 36 months acknowledging AFOSR support: 16

1. Ceramic-Reinforced Polymers and Polymer-Modified Ceramics, J. E. Mark, Polym. Eng. Sci., **36**, 2905 (1996).
2. Dynamic-Mechanical Thermal Analysis of Aramid-Silica Hybrid Composites Prepared in a Sol-Gel Process, Z. Ahmad, M. I. Sarwar, and J. E. Mark, J. Appl. Polym. Sci., **63**, 1345 (1997).
3. Chemically-Bonded Silica-Polymer Composites from Linear and Branched Polyamides in a Sol-Gel Process, Z. Ahmad, M. I. Sarwar, and J. E. Mark, J. Mats. Chem., **7**, 259 (1997).
4. Molecular Aspects of Rubberlike Elasticity, J. E. Mark and B. Erman, in "Polymer Networks", ed. by R. F. T. Stepto, Blackie Academic, Chapman & Hall, Glasgow, 1998.
5. Synthesis, Structure, and Properties of Hybrid Organic-Inorganic Composites Based on Polysiloxanes. 1. Poly(Dimethylsiloxane) Elastomers Containing Silica, D. W. McCarthy, J. E. Mark, and D. W. Schaefer, J. Polym. Sci., Polym. Phys. Ed., **36**, 1167 (1998).
6. Synthesis, Structure, and Properties of Hybrid Organic-Inorganic Composites Based on Polysiloxanes. 2. Comparisons Between Poly(Methylphenylsiloxane) and Poly(Dimethylsiloxane), and Between Titania and Silica, D. W. McCarthy, J. E. Mark, S. J. Clarson, and D. W. Schaefer, J. Polym. Sci., Polym. Phys. Ed., **36**,

7. High-Temperature Organic-Inorganic Hybrids, J. E. Mark, ICG XVIII American Ceramic Society Proceedings, San Francisco, 1998.
  8. Development of Some Promising Approaches for the Toughening of High-Temperature Polymers, C. Kumudinie, J. K. Premachandra, J. E. Mark, T. D. Dang, M. R. Unroe, and F. E. Arnold, in "Better Ceramics Through Chemistry VIII", ed. by C. J. Brinker, E. P. Giannelis, R. M. Laine, and C. Sanchez, Materials Research Society, Warrendale, PA, 1998.
  9. Silica-Reinforced Polymers and Polymer-Modified Silica, J. E. Mark, in "Silica from Synthesis to Application", ed. by B. Haidar, CNRS Proceedings Book, Mulhouse, France, 1998.
  10. Thermal and Mechanical Properties of Aramid-Based Titania Hybrid Composites, M. I. Sarwar, Z. Ahmad, and J. E. Mark, J. Appl. Polym. Sci., **70**, 297 (1998).
  11. Biomimetic Materials: Recent Developments in Organic-Inorganic Hybrids, Z. Ahmad and J. E. Mark, in special issue on "Organic/Inorganic Hybrid Materials", Mat. Sci. Eng.: C, Biomimetic Materials, Sensors, and Systems (ed. by J. E. Mark and P. D. Calvert), **6**, 183 (1998).
  12. Preparation and Properties of Some Hybrid Aerogels from a Sulfopolybenzobisthiazole-Silica Composite, J. K. Premachandra, C. Kumudinie, J. E. Mark, T. D. Dang, and F. E. Arnold, J. Macromol. Sci. - Pure Appl. Sci., **A36**, 73 (1999).
  13. Toughening of some high-temperature poly(arylene ether)s and a hydroxypoly(benzoxazole) by sol-gel generated rubbery particles, C. Kumudinie, J. K. Premachandra, J. E. Mark, T. D. Dang, M. R. Unroe and F. E. Arnold, submitted to Polymer.
  14. Toughening of Polyamides by the In-Situ Generation of Elastomeric Phases, Y. W. Park and J. E. Mark, manuscript in preparation.
  15. Toughening Poly(Biphenylethertriphenylphosphate) with Silica-Siloxane Phases via a Sol-Gel Process, W. Zhou, J. E. Mark, M. R. Unroe, and F. E. Arnold, manuscript in preparation.
  16. Toughening of Polyamides by Incorporation of Fumed Silica, Y. W. Park and J. E. Mark, manuscript in preparation.
- (7) Awards and Honors
- Special Research Fellow, National Institutes of Health  
Massachusetts Institute of Technology (Fall Term of 1975)  
Stanford University (Spring Term of 1976)
  - Best Paper and Honorable Mention Awards, American Chemical Society  
Rubber Division (1978, '75, '77)
  - Cincinnati Chemist of the Year, American Chemical Society (1984)
  - Distinguished Scientist Award, Technical Societies Council of Cincinnati (1985)
  - Rieveschl Award for Distinguished Scientific Research, University of Cincinnati, (1986)
  - George Stafford Whitby Award, American Chemical Society Rubber Division (1991)
  - American Chemical Society Award in Applied Polymer Science (1994)

Fellow of American Physical Society, New York Academy of Sciences, Graduate School of the University of Cincinnati, and American Association for the Advancement of Science  
Hans H. Jaffe Chemistry Faculty Award for Excellence, University of Cincinnati (1995)  
McMicken Dean's Award for Distinguished Scholarship, University of Cincinnati (1996)  
Charles Goodyear Medal, Rubber Division of the American Chemical Society (1999)

### 3. TRANSITIONS

- (a) PI: James E. Mark/Institution: University of Cincinnati (UC)
- (b) Samples of high-temperature polymers prepared at the Wright Patterson Air Force Base (WPAFB) were transitioned to the University of Cincinnati, where they were converted into toughened composites. The results obtained were interpreted jointly between the UC group and the WPAFB group, and the results were written up as joint publications. Four such papers are referenced as number 8, 12, 13, and 15 in the list given above.
- (c) Drs. Fred E. Arnold, Marilyn R. Unroe, Thuy D. Dang and  
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- (d) Presentations: American Chemical Society (Division of Polymer Chemistry), Dallas, March, 1998, and Materials Research Society, San Francisco, April, 1998 and April, 1999.
- (e) Applications: Structural materials in aircraft, and toughened higher-melting transparent polymers for aircraft canopies

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